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Gas sensing study of ZnO nanowire heterostructured with NiO for detection of pollutant gases

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Abstract

The use of metal oxide single crystalline nanowires for chemical sensing of pollutant gases has been proposed as a reliable solution to ensure high sensor performance due to small size of the crystallites and good stability over long term operation at high temperature. To obtain enhanced sensing capabilities of ZnO nws, we prepared composite nanostructures based on p-type NiO and n-type ZnO NWs that combine the different physical and chemical properties of individual components. The superior functional performances are demonstrated in the current work by testing functional properties of chemical sensors towards reducing and oxidizing gases. The ZnO/NiO heterostuctures showed better relative response towards acetone and ethanol, with a decrease in response and recovery times with respect to uncoated ZnO nws. This is especially evident at 400°C and for a determined thickness of the NiO layer.

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Keywords: NiO; ZnO nanowires; heerostuctures; acetone; SEM; Raman.

1. Introduction

Pollution and its effects on health and safety is a concern from several years: this is expanding the research on chemical sensors. Among metal oxide gas sensors, quasi one dimensional nanostructures have several advantages

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with respect to thin- and thick film counterpart such as large surface-to-volume ratio, lateral dimensions comparable to the surface space charge region, and superior stability when in the single crystal structure [1,2]. They can be operated at high temperature with an excellent stability and their surface can be functionalized with catalyzers. Current years have seen increased interests in the synthesis of p/n metal oxide-based nanocomposites and their great potential in advanced applications, such as optoelectronics, photosensors [3] and gas sensors [4]. The fabrication of composite nanostructures based on the combination of p-type and n-type semiconducting oxides offers an important path to combine the different physical and chemical properties of individual components into one system. The superior functional performances of these systems in comparison to the corresponding single-phase metal oxides are ascribed to the build-up of an inner electric field at the p/n junction interface [5, 6], and to the sensing capabilities of the selected metal oxides. In this communication we combined ZnO nanowires (nws) to NiO porous layer by sputtering and determined the preparation conditions necessary to obtain an enhancement of the sensing response and of the response and recovery times.

2. Experimental

NiO-ZnO heterostructures were obtained by vapor phase growth of ZnO nws followed by NiO thin layer deposition by RF sputtering.

ZnO NWs were grown using a vapour phase growth technique. Zinc oxide powder was placed on an alumina crucible at a temperature of 1200°C at 10 mbar to induce its evaporation. Pt catalyst was used to induce the deposition of nanowires onto alumina substrates.

Nickel oxide thin films were deposited by RF magnetron sputtering on ZnO nws starting from a nickel oxide target (99.99% pure, 4" size from CERAC), keeping the substrates at room temperature. Gas pressure was 10^{-2} mbar (50%Ar/50%O_2) and the power was 100W. Deposition time was changed from 15 to 30 minutes to obtain a layer with nominal thickness of 40 nm and 80 nm, labeled as ZnO nws/NiO1 and ZnO nws/NiO2. As a benchmark material, uncoated ZnO nws sensors were used.

The sensing heterostructures were prepared on 2 mm × 2 mm alumina substrates for gas sensing and SEM characterization. Interdigitated Pt contacts and a backside Pt heater were deposited by sputtering after the deposition of the sensing layers. Aging at 500°C for two week was applied prior to sensing measurements. The tests were performed by a volt amperometric technique at constant bias (1V). The system used to dynamically reproduce environmental conditions in a controlled and repeatable way is based on volumetric mixing through mass flow controllers and certified bottles. All characterizations were performed keeping the ambient at a temperature of 20°C, at atmospheric pressure, and at 50% relative humidity (RH). Reducing and oxidizing gases like ethanol, acetone, CO and NO_2 at 50% RH were tested. The working temperature range was investigated from 300°C to 500°C.

3. Results and discussions

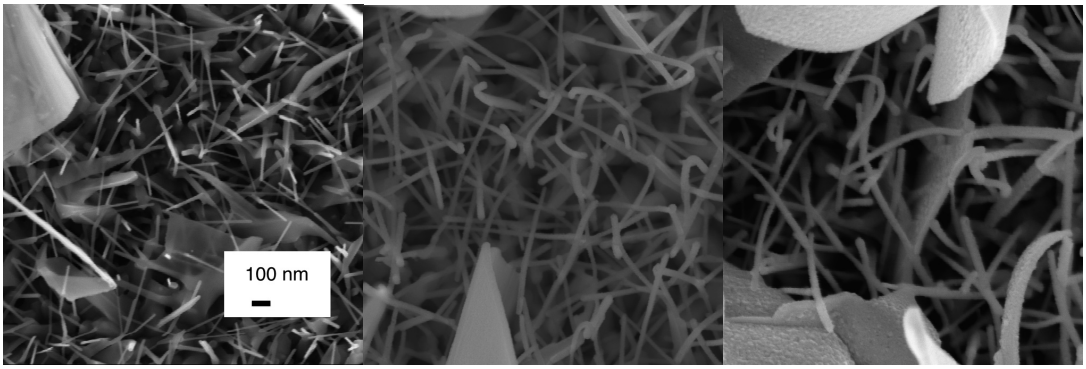

Fig. 1. SEM images taken at 100KX magnification of: (Left) ZnO nanowires; (b) ZnO nanowires with 40 nm NiO;(c) ZnO nanowires with 80 nm NiO. The marker is the same for the three images.

The surface morphology of the nanostructured sensors was investigated by Field Emission-SEM at 10keV accelerating voltages at 100KX magnification. Figure 1 showed the morphology of ZnO nws, compared to the ones of NiO/ZnO heterostructures. ZnO sample (Figure 1-Left) is composed by very thin nwss with diameter in the range of 10-20 nm and by crystalline platelets dispersed over the nanowire forest. The nanowires are randomly oriented. ZnO nws/NiO1 sample (Figure 1-Center) showed an increased diameters of the wires (30-40 nm), that seems to be covered by a porous layer of NiO. The same is true for platelets, were the porous structure is evident at 200KX magnification (not shown here). ZnO nws/NiO2 sample (Figure 1-Right) shows similar morphology to the previous sample, but the porous layer of NiO appears to be thicker on wires and on platelets. Bending of the wires can also be observed in the heterostructured samples either due to the kinetic energy of the sputtered atoms or to the weight of NiO layers on the thin ZnO wires. The platelets that are semi-transparent in the ZnO sample are covered by non-transparent NiO layer in the heterostructured sensors.

Figure 2 reports the dynamic response of the tested sensors at all temperatures. ZnO nws and NiO/ZnO heterostuctures showed n-type behavior independently from NiO amount. The presence of NiO layer on ZnO nws ensures better response towards oxidizing and reducing gases at all temperatures as shown in Fig. 2. Response to NO_2 was observed for temperatures lower than 300°C, while response to ethanol and acetone increases with optimum working temperatures at 500°C. While the effect of increasing the sensor response is evident at all temperatures, the decrease in the response and recovery times is better observed at 400°C. Fig. 3 reports the normalized current of the three different sensors towards acetone (50 ppm) at 400°C: a 3-fold enhancement in sensing response was observed for NiO/ZnO heterostructures with lower NiO thickness (ZnO/NiO1). Recovery times reduce from 960s for ZnO nws to 270s for ZnO nws/NiO1 and to 210 s for ZnOnws/NiO2.

All sensors showed n-type behaviour: reducing gases interact with oxygen ionosorbed at the sensor surface, releasing electrons into the conduction band and thus increasing current [7]. In our case it is most probable that current flows into ZnO nws and NiO porous material contribute to enhancement of sensing properties by two factors: the creation of a p-n junction at the interface that enhances depletion of the ZnO nws, and increased oxygen ionosorption on the surface of NiO with respect to ZnO [8].

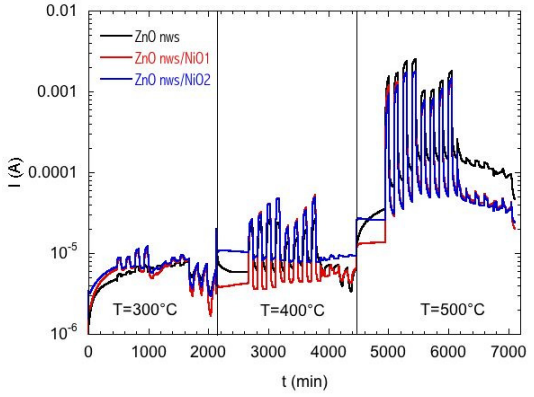

Fig. 2. : Dynamic response of sensors at 300°C-400°C and 500°C towards ethanol (100-100-300-500 ppm), acetone (25-25-50-100 ppm) and NO_2 (1-1-5-8 ppm).

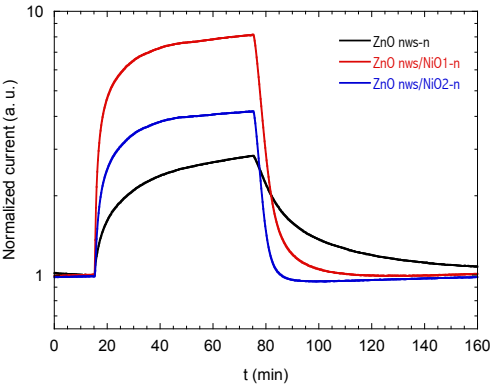

Fig. 3: Dynamic response at 400°C of different sensors. The sensors' current was normalized for comparison.

4. Conclusions

We were able to prepare new sensing heterostructures based on ZnO nanowires prepared by vapour phase growth covered by NiO layer deposited by RF sputtering at different thickness. From SEM analysis we observed that NiO effectively forms a porous layer on the ZnO nanowires, uniformly coating them; the porous layer is more evident for higher NiO amount used in this work. Functional tests towards reducing and oxidizing gases in the temperature range between 300°C and 500°C showed increasing in sensor response towards acetone and ethanol for the lower nominal thickness used. The response and recovery times are also reduced for all NiO/ZnO heterostructures with respect to ZnO nws, especially at 400°C.

Acknowledgements

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